



## Vaterite calcium carbonate for the adsorption of Congo red from aqueous solutions



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### ABSTRACT

The present study describes the evaluation of vaterite calcium carbonate ( $\text{CaCO}_3$ ) for the adsorption of Congo red (CR) from aqueous solution. Vaterite  $\text{CaCO}_3$  is produced via a precipitation method assisted by ethylene glycol (EG), which acts as stabilizer to prevent transformation of vaterite to others polymorphs of  $\text{CaCO}_3$ . The crystal structure of vaterite  $\text{CaCO}_3$  formed was proven by SEM, XRD and FTIR. The highest zeta potential of the vaterite  $\text{CaCO}_3$  was 15.2 mV, which was obtained at pH 5. Batch adsorption studies illustrated that the adsorption of CR to the vaterite  $\text{CaCO}_3$  was dependent on different parameters, such as pH, initial dye concentration and temperature. The adsorption isotherm data were highly consistent with Langmuir isotherm model, while the adsorption kinetics data fitted better to the pseudo-second-order model. The maximum adsorption capacity of the  $\text{CaCO}_3$ , 32.60 mg/g, was obtained from the adsorption kinetic experiment under adsorption conditions, pH 5, adsorbent dose 0.2 g, adsorbate concentration 100 mg/L and temperature 25 °C. The adsorption of CR on the  $\text{CaCO}_3$  was proven to be endothermic and non-spontaneous in nature.

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### Introduction

Most dyes used in industries are of synthetic chemical compounds with complex aromatic structures [1]. Synthetic dyes are widely used in various industries, including textile, rubber, paper, plastic, cosmetic, paint, leather, food, and pharmaceutical [2]. Azo dyes are popular and widely used in textile industry [3]. They can cause environmental pollution problems by forming hazardous aromatic amines through metabolic processes in plants and animals. They can cause carcinogenic and mutagenic effects in animal even at low concentration [4]. Azo dye can also cause coloration on the surface of water, which would block the penetration of sunlight and decrease oxygen levels in water. Moreover, azo dyes are difficult to be degraded via biodegradation and photocatalysis due to their complex and stable aromatic molecular structures [3].

There are various treatment processes for the removal of dyes from wastewater, such as adsorption, coagulation, oxidation, membranes separation, etc. [5]. Amongst, adsorption is one of the effective, simple and economical methods to remove different

types of pollutants from wastewater. There are various types of inorganic particles which have been used as adsorbent for the removal of dyes and heavy metal ions from aqueous solutions, such as  $\text{MnO}_2$  [6] and kaolinite [7] used for removal methylene blue (MB),  $\text{Ni}(\text{OH})_2$  and NiO for the removal of Congo red (CR) [8].

$\text{CaCO}_3$  is one of the most abundant minerals on Earth. It has been used as filler in many consumer products, such as paint, plastic, rubber, paper, printing ink, toothpaste, cosmetics and food [9], due to its low cost, excellent physical and chemical characteristics, biocompatibility, biodegradability, etc. [10]. Besides,  $\text{CaCO}_3$  has been used to remove fluoride [11] and heavy metals from water [12]. There are three types of anhydrous crystalline polymorphs of  $\text{CaCO}_3$ , i.e., calcite, aragonite, and vaterite [9]. Vaterite is a less stable polymorph which can be transformed easily into a thermodynamically stable form of calcite [13]. However, the excellent properties of vaterite, including high specific surface area, high dispersivity, and low specific gravity, make it widely used in many applications compared to the two others [14].

In this study, vaterite  $\text{CaCO}_3$  is produced via wet precipitation method using ethylene glycol (EG) as stabilizer. The produced  $\text{CaCO}_3$  was used as adsorbent to remove CR from aqueous solution. The effects of different parameters, such as pH, temperature and dye concentration, on the adsorption performance of the  $\text{CaCO}_3$  were investigated.

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## Materials and methods

### Chemicals

Calcium chloride ( $\geq 96.0\%$ ,  $\text{CaCl}_2$ ) and sodium carbonate ( $\geq 99.5\%$ ,  $\text{Na}_2\text{CO}_3$ ) were purchased from Sigma–Aldrich (Japan). Ethylene glycol (EG, 99.5%,  $M_w = 62.07$  g/mol) was purchased from System (Malaysia). Congo red (pure grade,  $\text{C}_{32}\text{H}_{22}\text{N}_6\text{O}_6\text{S}_2 \times 2\text{Na}$ ,  $M_w = 696.7$ ) was purchased from Acros (USA). All chemicals were of analytical grade and used without further purification. Hydrochloric acid (37%, HCl) was purchased from Merck (Germany) while sodium hydroxide (NaOH, 99.0%,  $M_w = 40.0$  g/mol) was purchased from R&M Chemical (UK).

### Measurements of CR concentration

Concentration of CR in aqueous solution was analyzed using a UV–vis spectrophotometer (Jenway 7315 Spectrophotometer). Standard solutions of CR with different concentrations, ranging from 10 to 100 mg/L, were scanned at a  $\lambda_{\text{max}}$  of 500 nm and the absorbance intensity was used to prepare a calibration curve according to Beer–Lambert's law, as shown in Fig. S1. This calibration curve was used to determine the concentration of CR after adsorption experiment.

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### Synthesis of vaterite $\text{CaCO}_3$

A EG solution (20 vol%) was prepared using deionized water. Then, 0.5 M  $\text{CaCl}_2$  and 0.5 M  $\text{Na}_2\text{CO}_3$  were prepared using the EG solution. Both solutions were mixed in a beaker and stirred at room temperature (20 °C) by using a magnetic stirrer for 60 min. The precipitated  $\text{CaCO}_3$  was filtered, washed with deionized water, and dried in a freeze dryer (ScanVac CoolSafe).

### Characterizations of the $\text{CaCO}_3$

Micrograph of the  $\text{CaCO}_3$  sample was taken by a variable pressure scanning electron microscope (VPSEM LEO 1450VP) at 30 keV. The crystalline phase and structure of the synthesized  $\text{CaCO}_3$  were detected by an X-ray diffractometer (XRD) Bruker D8-Advance. Fourier transform infra-red spectroscopy (FT-IR) analysis was performed on a PerkinElmer Spectrum 400 FT-IR NIR. Zeta potential,  $\zeta$ , of the  $\text{CaCO}_3$  at different pHs was analyzed using a Malvern Zetasizer Nano ZS. Deionized water with different pHs (5, 7, and 9) was prepared using 0.1 M HCl and 0.1 M NaOH. About

20 mg of  $\text{CaCO}_3$  powder was weighted and added into the deionized water for each measurement.

### Adsorption studies of CR on $\text{CaCO}_3$

#### Effect of pH on adsorption

Adsorption experiments were conducted to investigate the effect of initial pH ( $\text{pH}_0 = 3, 5$  and 7) of the CR solution on the adsorption capacity of the  $\text{CaCO}_3$ . All the experiments were carried out at 20 °C using 0.2 g  $\text{CaCO}_3$  in 100 mL CR (100 mg/L). The pH of the CR solution was adjusted using 0.1 M HCl and 0.1 M NaOH. The mixture was left to stir at 300 rpm using an overhead stirrer for 3 h to achieve adsorption equilibrium. The concentration of CR was measured using the UV–vis spectrophotometer at  $\lambda_{\text{max}}$  of 500 nm. The adsorption capacity,  $q_e$  (mg/g), of the  $\text{CaCO}_3$  was calculated using Eq. (1):

$$q_e = \frac{C_0 - C_e V}{m} \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium concentration of CR (mg/L), respectively.  $V$  is the volume of the CR solution (L) and  $m$  is the mass of the  $\text{CaCO}_3$  (g).

#### Batch adsorption kinetics

To study the adsorption kinetics of CR on the  $\text{CaCO}_3$ , the mixture of  $\text{CaCO}_3$  and CR was stirred at 300 rpm using the overhead stirrer. A 0.2 mL aliquot sample was withdrawn at various time intervals, i.e., 10, 20, 30, 45, 60, 90, 120, 150 and 180 min. The aliquot was centrifuged at 12,000 rpm for 10 min. The concentration of CR adsorbed at time  $t$ ,  $q_t$  (mg/g), was calculated using Eq. (2):

$$q_t = \frac{C_0 - C_t V}{m} \quad (2)$$

where  $C_t$  is the concentration of CR at time,  $t$  (mg/L).

#### Adsorption isotherms

Adsorption isotherm experiments were conducted using 30 mg of  $\text{CaCO}_3$  and 15 mL of CR solution with different initial CR concentrations, i.e., 25, 50, 100, 200 and 300 mg/L, in glass vials at different temperatures (25, 40 and 60 °C) for 4 h using a water bath shaker. The mixture was then centrifuged at 12,000 rpm for 10 min, and the concentration of CR at the adsorption equilibrium was analyzed by the UV–vis spectrophotometer.

## Results and discussion

### Characterization of $\text{CaCO}_3$

#### SEM

Fig. 1 shows a SEM image of the produced  $\text{CaCO}_3$ . As can be seen that the  $\text{CaCO}_3$  is in spherical shape with an average diameter

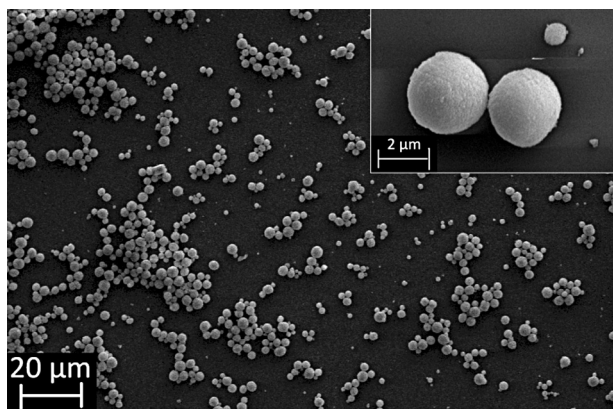


Fig. 1. SEM image of vaterite  $\text{CaCO}_3$  synthesized in the presence of EG. The inset is the vaterite particle at 10 $\times$  magnification.

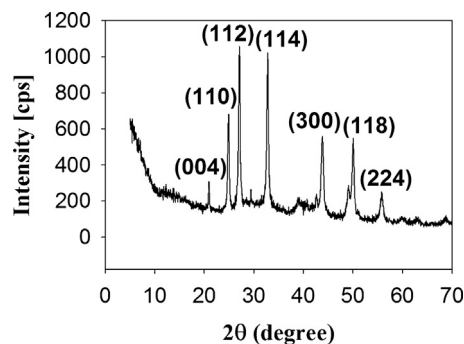


Fig. 2. XRD pattern of vaterite  $\text{CaCO}_3$ –EG.

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